

AD 607616

FIRST ANNUAL REPORT

Nour 4217(00)

ARPA Order No. 442, Item 3

Program Code No. 3910

NEW HYPOFLUORITES CONTAINING NITROGEN

University of Idaho  
Moscow, Idaho

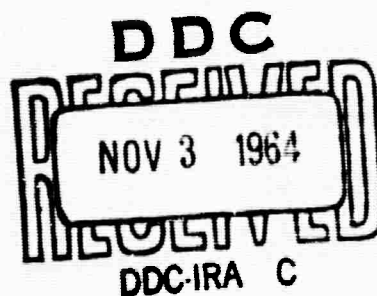
Jean'ne M. Shreeve

|            |          |    |   |       |
|------------|----------|----|---|-------|
| COPY       | 2        | OF | 3 | Myman |
| HARD COPY  | \$ .1.00 |    |   |       |
| MICROFICHE | \$ .0.50 |    |   |       |

1 October 1964

9p

Reproduction in whole or in part is permitted for any  
purpose of the United States Government.



**BEST  
AVAILABLE COPY**

### Abstract

Attempts to prepare  $\text{NF}_2\text{OF}$  by (1) the fluorination of nitric oxide; (2) the reaction of  $\text{N}_2\text{F}_4 + \text{HgO}$ ; and (3) the catalytic fluorination of  $\text{NF}_2\text{OSO}_2\text{F}$ , have been unsuccessful. Some preliminary data on the thermal decomposition of  $\text{NF}_2\text{OSO}_2\text{F}$  are included.

Catalytic fluorination of trifluoronitrosomethane has yielded  $(\text{CF}_3)_2\text{NOCF}_3$  which has been more completely characterized and very likely  $\text{CF}_3(\text{F})\text{NOCF}_3$  is also produced. As the other member of this series,  $\text{NF}_2\text{OCF}_3$  has been prepared and partially characterized.  $(\text{CF}_3)_2\text{NOCF}_3$  is stable to at least  $200^\circ$  even in the presence of equimolar amounts of elemental fluorine. The thermal decomposition of  $\text{CF}_3\text{C}(\text{O})\text{ONO}$  also gives  $(\text{CF}_3)_2\text{NOCF}_3$  in about 5% yields.

## FIRST ANNUAL REPORT

### Attempted Preparation of $\text{NF}_2\text{OF}$

#### Fluorination of nitric oxide

##### A. Static Reactor

Known amounts of nitric oxide were frozen into an 8 ml. monel tube equipped with a No. 413 Hoke valve and containing  $\text{AgF}_2$ . Fluorine was condensed on the nitric oxide at liquid nitrogen temperature reactions to be observed with either NO or  $\text{F}_2$  in excess. An excess of fluorine was the usual case. The mixture was allowed to warm slowly to room temperature and to remain at this temperature for several hours. Unreacted fluorine was removed by pumping on the mixture at  $-196^\circ$ . The products which are non volatile at this temperature were separated by fractional codistillation (1) and identified with infrared. Total pressure in any reaction ranged between twelve and 85 atmospheres. Contact time was in excess of 15 hours. In every case, the products identified were:  $\text{FNO}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}_3$ .

##### B. Flow reactor

Fluorine at about 6 l/hour, with nitrogen as a diluent, was caused to flow over nitric oxide in a brass vessel held at  $-196^\circ$ . During this flow the brass vessel was allowed to warm slowly to room temperature. The gases were condensed in a glass trap at  $-183^\circ$ . Products were identified as:  $\text{SiF}_4$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$  and traces of  $\text{FNO}$ .

##### C. Flow reactor with $\text{AgF}_2$ catalyst (2)

Nitric oxide was mixed with nitrogen and combined with fluorine in a  $\text{AgF}_2$  catalytic flow reactor. Products were trapped in a brass trap at  $-196^\circ$ . Fluorine was kept in excess at all times, with a flow rate of 4 l/hr while the nitric oxide was varied from 14 ml/min to 31 ml/min. Products obtained at 25, 150 or 170° after a residence time of about 15 minutes were:  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$  and  $\text{FNO}$ .

## II. Tetrafluorohydrazine + mercury(II) oxide

### A. Room temperature

Tetrafluorohydrazine at 40 mm pressure was admitted to a flask containing about two grams of previously dried yellow mercury(II) oxide and was allowed to remain in contact for 0.5 hr. Only  $N_2F_4$  was recovered.

### B. 96°

The  $N_2F_4$  from above was returned to the reaction vessel and the temperature was increased to 96° for one hour. Infrared spectra showed:  $NO_2$ ,  $SiF_4$  and  $NF_3$ .

### C. Ultraviolet radiation

To a one liter Pyrex bulb which contained 2 grams of  $HgO$ ,  $N_2F_4$  was added until the pressure was 165 mm. The mixture was treated with ultraviolet radiation for 8 hours. Infrared spectra showed:  $NO_2$ ,  $SiF_4$  and  $NF_3$ .

Conclusion. Although contacting yellow  $HgO$  with elemental chlorine at room temperature permits the preparation of good yields of  $Cl_2O$ , the similar reaction does not seem to occur between  $N_2F_4$  and  $HgO$ .

## III. Fluorination of N,N-Difluoro-O-fluorosulfatohydroxylamine

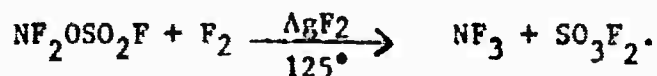
N,N-Difluoro-O-fluorosulfatohydroxylamine was prepared as described by Lustig and Cady (3).

### A. Ultraviolet radiation.

Ultraviolet radiation for two hours of a 2:1 mixture of  $NF_2OSO_2F$  and fluorine at a total pressure of one atmosphere in a flask equipped with a quartz finger brought no reaction.

### B. Fluorination of the amine in a catalytic flow reactor.

The procedure was to carry the  $NF_2OSO_2F$  with nitrogen at the rate of 10 ml/min. into the reactor where it was mixed with an excess of fluorine at 125°. The products were trapped in glass and separated using fractional codistillation (1). The main reaction is given by



however, large amounts of  $\text{SO}_2\text{F}_2$  and smaller quantities of an unidentified low-boiling compound with a strong infrared absorption at 10.5 microns were obtained, also. The same reaction was run in the presence of a  $\text{CuF}_2$  catalyst. In this case, only  $\text{NF}_3$  and  $\text{SO}_3\text{F}_2$  were identified.

Investigation is continuing in this area and reaction will be examined at temperatures lower than  $25^\circ$  and also at high pressure (ca. 100 atmospheres).

#### V. Thermal decomposition of N,N-Difluoro-O-fluorosulfatehydroxylamine

All decompositions were carried out isothermally in two one-liter brass cans which had been fluorinated at temperatures in excess of  $150^\circ$ . One was packed with copper gauze. The cans were thermostated in a Fischer Isotemp Junior model gravity-convection oven, whose temperature, as measured by chromel-alumel thermocouples, was observed never to vary more than  $\pm 0.25^\circ$  at equilibrium. Initial and final pressures were obtained with a mercury manometer. The products, after decomposition, were trapped in glass tubes held at  $-183^\circ$ , separated via fractional codistillation and identified from infrared spectra. The data given below are preliminary and this study is continuing in a new all metal system equipped with a Bourdon-type pressure indicating device.

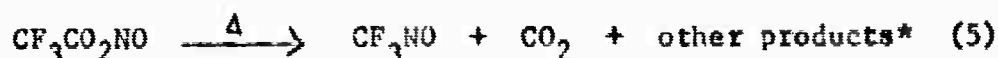
Some decompositions were run at temperatures between 100 and  $200^\circ$ .

| $\text{NF}_2\text{OSO}_2\text{F}$<br>mm | T<br>° C | Time<br>hr | Reactor<br>type | Products  |
|---|----------|------------|-----------------|---|
| 38                                      | 105      | 3          | packed          | $\text{NF}_2\text{OSO}_2\text{F}$ + trace ( $\text{SO}_2\text{F}_2$ , $\text{N}_2\text{F}_4$ , $\text{S}_2\text{O}_5\text{F}_2$ )                                   |
| 29                                      | 153      | 3          | packed          | $\text{N}_2\text{F}_4$ + small amts. ( $\text{NF}_3$ , $\text{NF}_2\text{OSO}_2\text{F}$ , $\text{SO}_2\text{F}_2$ , $\text{S}_2\text{O}_5\text{F}_2$ )             |
| 73                                      | 175      | 2.5        | unpacked        | $\text{N}_2\text{F}_4$ + small amts. ( $\text{SO}_2\text{F}_2$ , $\text{S}_2\text{O}_5\text{F}_2$ , $\text{NF}_2\text{SO}_3\text{F}$ ) + trace $\text{N}_2\text{O}$ |
| 122                                     | 198      | 2          | unpacked        | $\text{N}_2\text{F}_4$ + $\text{SO}_2\text{F}_2$ + $\text{S}_2\text{O}_5\text{F}_2$ + trace ( $\text{NF}_2\text{OSO}_2\text{F}$ , $\text{N}_2\text{O}$ )            |

Because of the variety of products and nonreproducibility of the decomposition curve and because of increasing interest in other projects, the decomposition was temporarily abandoned but is now being considered again.

#### Fluorination of trifluoronitrosomethane.

Trifluoronitrosomethane may be prepared in good yield by the following:



\* Other products are discussed below.

A glass trap containing a known amount of  $\text{CF}_3\text{NO}$  in a Dewar was allowed to warm slowly from  $-183^\circ$  as nitrogen was bubbled through. The  $\text{CF}_3\text{NO}$  was mixed with an excess of fluorine immediately prior to entering the  $\text{AgF}_2$  catalytic reactor. The products were caught in a glass trap at  $-183^\circ$ . Fluorine was passed through an HF scrubber before entering the reactor.

Preliminary separation of products was made using a dry ice-acetone bath which permitted the most volatile materials to be collected in a second trap at  $-183^\circ$ . Products in each of the traps were separated using either fractional codistillation or a 10-foot column filled with Kel-F adsorbed on Chromasorb P at  $-25^\circ$ .

| Run | mM $\text{CF}_3\text{NO}$ | mM $\text{C}_2\text{F}_6$ | mM $\text{COF}_2$ | T<br>°C | $\text{F}_2$<br>l/hr | $\text{N}_2$<br>ml/min |
|-----|---------------------------|---------------------------|-------------------|---------|----------------------|------------------------|
| 1   | 9.9                       | 0.9                       | 0.2               | 24      | 1.2                  | 33                     |
| 2   | 9.9                       | 0.9                       | 0.2               | 57      | 1.0                  | 33                     |
| 3   | 51.9                      | 4.7                       | 1.7               | 128     | 1.0                  | 33                     |

| Reaction Products              | Run 1 | 2     | 3      |
|--------------------------------|-------|-------|--------|
| $\text{CF}_4$                  | 6%    | 5.54% | 31.0%  |
| * $\text{C}_2\text{F}_6$       | -     | -     | 6.0    |
| * $\text{COF}_2$               | -     | -     | 2.41mM |
| $(\text{CF}_3)_2\text{NF}$     | 12.7  | 2.72  | 9.3%   |
| U-V                            | 2.4   | 0.71  | 3.45   |
| $(\text{CF}_3)_2\text{NOCF}_3$ | 6.4   | 14.7  | 14.9   |
| $\text{CF}_3\text{OF}^2$       | trace | -     | 0.13mM |
| $\text{NF}_3$                  | trace | -     | trace  |
| $\text{FNO}$                   | -     | -     | trace  |

\* Amount in excess of that present in the starting material. Amounts of  $\text{NO}_2$ ,  $\text{SiF}_4$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were not measured.

A. The compound labeled, U-V, appears to be  $\text{CF}_3(\text{F})\text{NOCF}_3$ . This has not been entirely confirmed pending mass and NMR spectra. Infrared absorptions occur at: 1360, 1300, 1230 1190, 995, and 735  $\text{cm}^{-1}$ .

Bis(trifluoromethyl)trifluoromethoxyamine.

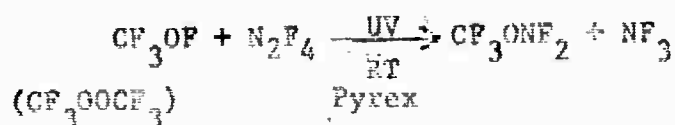
The compound  $((CF_3)_2NOCF_3)$  has been reported by Yakulovich (6). It has been more completely characterized in this laboratory. Extrapolation of a vapor pressure curve indicates a boiling point of  $3^\circ$  (compared to  $3.5^\circ$ ). Experimental molecular weights are an average of 232 compared to the calculated 237. Elemental analyses, mass and NMR spectra are in accord with  $CF_3NOCF_3$ . It is a colorless gas which oxidizes iodide to iodine. Infrared absorptions occur at 1300, 1270, 1220, 1190, 1075, 980, 720 and  $690\text{ cm}^{-1}$ .

The thermal stability of  $(CF_3)_2NOCF_3$  was examined by heating the compound slowly from room temperature to  $200^\circ$  in a fluorinated one-liter brass reactor.

| Run | Initial Pressure                               | Max. Temp. $^\circ\text{C}$ | Time at Highest T | Pressure-Temp. Curve       |
|-----|--|-----------------------------|-------------------|----------------------------|
| 1   | $(CF_3)_2NOCF_3$<br>21 mm                      | 200                         | 24                | Ideal Gas                  |
| 2   | $(CF_3)_2NOCF_3 + N_2 + F_2$<br>1:1:1<br>99 mm | 200                         | 16.5              | Ideal Gas<br>(no reaction) |

Earlier in this work, fluorinations of  $CF_3NOF$  were run, but since essentially the same compounds were obtained as with  $CF_3NO$ , this was not pursued.

With the preparation of  $CF_3(CF_3)NOCF_3$  and  $CF_3(F)NOCF_3$ , it seemed of interest to attempt the preparation of  $F_2NOCF_3$ . This was easily accomplished by the ultraviolet irradiation of an equimolar mixture of either bis(trifluoromethyl)peroxide  $(CF_3OOCF_3)$  or trifluoromethyl hypofluorite  $(CF_3OF)$  and tetrafluorohydrazine



Fluoro(trifluoromethoxy)amine is a colorless gas at room temperature with a boiling point of  $-60^\circ$ . An average experimental molecular weight of 140 was obtained relative to the calculated value of 137. The infrared spectrum has absorptions at 1305, 1240, 1030, 940, 875, and  $720\text{ cm}^{-1}$ . Mass and NMR spectra are being obtained.



### Pyrolysis of trifluoroacetyl nitrite.

Pyrolysis of trifluoroacetyl nitrite by passing the nitrogen-carried compound through a glass tube (2 x 28 cm) in an air thermostat (190-192°C) at the nitrogen flow rate of 100 ml/minute not only gives rise to good yields of the blue  $\text{CF}_3\text{NO}$  but also several other interesting products.

$(\text{CF}_3)_2\text{NOCF}_3$  is obtained in approximately 5% yields. Also included are  $\text{COF}_2$ ,  $\text{C}_2\text{F}_6$ ,  $\text{SiF}_4$ ,  $\text{NO}_2$ ,  $\text{CF}_3\text{NO}_2$  and two other compounds which have not been identified. Infrared spectra indicate a carbonyl group in one but not in the second. Work is continuing here.

### Reaction of carbon monoxide and tetrafluorohydrazine.

Carbon monoxide and  $\text{N}_2\text{F}_4$  were mixed and subjected to a variety of reaction conditions with addition of two difluoroamino groups or one difluoroamino and one fluoro group to the carbon monoxide as the desired reaction products.

Actually Ruff (7) has reported the preparation of the  $\text{CF}_3\text{NO}$  isomer,  $\text{FCOF}_2$  as a result of the fluorination of  $\text{AgCN}$ . Preliminary investigation of the  $\text{CO}-\text{N}_2\text{F}_4$  reaction is incomplete and inconclusive, but results are very promising when conditions of low-pressure and high-intensity ultraviolet radiation are applied. Work is rapidly progressing here.

#### BIBLIOGRAPHY

- (1) G. H. Cady and D. P. Siegworth, *Anal. Chem.*, 31, 618 (1959).
- (2) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, 70, 3986 (1948).
- (3) M. Lustig and G. H. Cady, *Inorg. Chem.*, 2, 388 (1963).
- (4) D. E. Rice and G. H. Crawford, *J. Org. Chem.*, 28, 872 (1963).
- (5) C. W. Taylor, T. J. Brice and R. L. Wear, *ibid.*, 27, 1064 (1962).
- (6) A. Ya. Yakubovich et. al., *Doklady Akad. Nauk SSSR*, 141, 125 (1961).
- (7) O. Ruff and M. Giese, *Chem. Ber.*, 69, 684 (1936).